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CALCULATION OF THE STATISTICAL SUMS FOR DIATOMIC
MOLECULES TAKING INTO ACCOUNT THE HIGHLY
EXCITED ELECTRON STATES

R. I. Artym

Translation of "Vychisleniye statisticheskikh summ dvukhatomnykh molekul
s uchetom vysokikh возбужденных электронных состояний."
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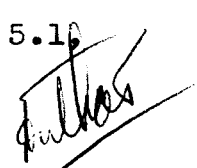
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R. I. Artym

ABSTRACT

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Calculations of the contributions to the statistical sum of the 41 electron states with excitation energies above $90,000 \text{ cm}^{-1}$ has been made for N_2 by means of the method proposed earlier. It has been found that at $20,000^\circ \text{ K}$ the contributions calculated in percent of the statistical sums of the ground state are correspondingly 5.1, 21.7, and 64.8 percent.



In the previous work (ref.1) we proposed an approximate method of computing the statistical sum of excited electron states using the approximation of the anharmonic oscillator -- of a rigid rotor taking into account the limitations of oscillatory and rotational states. As a practical example it is rational to apply this method to the calculation of statistic sums of excited electron states for the N_2 molecule. It is known that information on the thermodynamic

properties of molecular nitrogen at high temperatures is an extremely important problem in the most diverse fields of science and technology. In addition to this molecular nitrogen belongs to those substances which have undergone the most complete spectroscopic analysis.

Figure 1 shows the diagram for the energy levels of the N_2 molecule. The diagram shows more than 50 stable electron states and 15 systems of bands which have been investigated most completely. The excited state $a^1\pi_g$ was studied during the investigation of the system of bands named after Leiman, Berge, and Hopfield. On the diagram the energy levels for the state are taken from the data obtained by Lofthus (ref.2). The energy of excitation of state $a'^1\Sigma_u^-$ is determined as a result of investigations (performed in the vacuum ultraviolet region) of the forbidden transition $a'^1\Sigma_u^- \rightarrow X^1\Sigma_g^+$ in absorptions by Wilkinson and Mulliken (ref.3) and in emission by Ogawa and Tanaka (ref.4). The oscillatory levels of the state $a'^1\Sigma_u^-$ on the diagram are shown according to the data of Lofthus (ref.5). The energy of excitation of state $w^1\Delta_u$ is determined from the known energy of excitation for state $a'^1\Sigma_u^-$ and transitions associated with the bands of Kaplan (ref.5, 6). The oscillatory levels for the state $w^1\Delta_u$ in the diagram are recorded to the data of Lofthus and Mulliken (ref.6). The spectroscopic constants of the triple states $A^3\Sigma_u^+, B^3\Pi_g, C^3\Pi_u$ have been studied well due to the result of the investigations of the first and second positive systems of nitrogen in the visible and near ultraviolet region of the spectrum. The energies of excita-

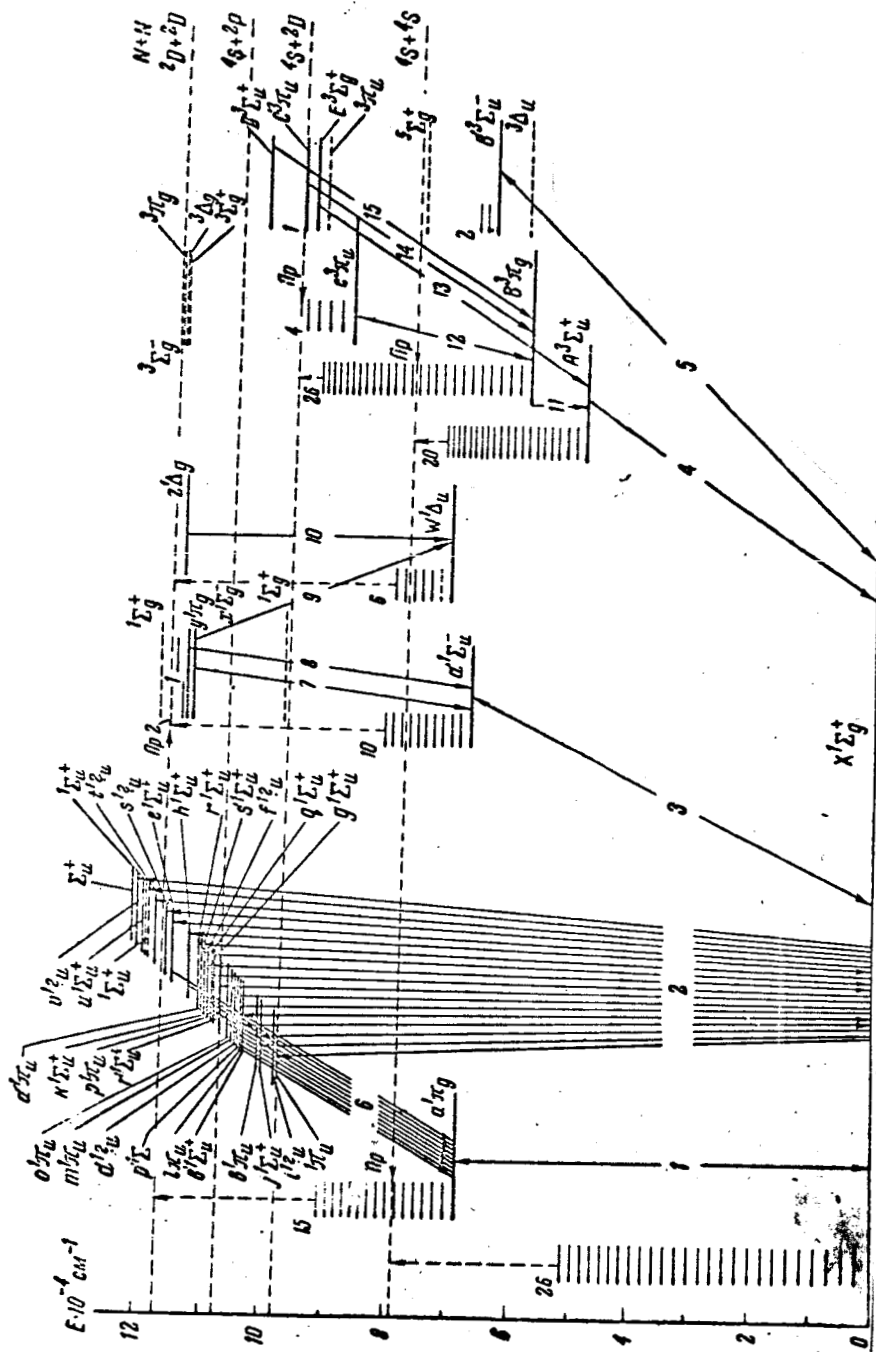


Figure 1. Schematic representation of levels of energy of N_2 molecule. Electron states are designated by heavy horizontal lines; electron states not observed experimentally by thin horizontal lines. The thinner shorter lines correspond to oscillatory levels. Numbers on the left indicate number of observed levels in a given state. Dissociation limits of electron states are designated by horizontal broken lines and vertical broken arrows. Short horizontal arrows represent observed boundaries of predissociation. Electron transitions observed in the N_2 spectrum are designated by solid arrows, where 1 is the system of Leiman-Berge-Hopfield bands, 2, system of Vegard-Kaplan bands, 3, system of Gaydon bands, 4, system of Herman-Kaplan bands, 5, system of Goldstein-Kaplan bands, 6, system of Herman-Kaplan bands, 7, first, second, fourth, and fifth positive systems of bands, 8, system of Lofthus bands, 9, first and second systems of Herman-Kaplan bands, 10, system of Goldstein-Kaplan bands, 11, 12, 13, system of Herman-Kaplan bands, 14, system of Goldstein-Kaplan bands, 15, system of Herman-Kaplan bands.

tion of the triple states $A^3\Sigma_u^+$, $B^3\Pi_g$ and $C^3\Pi_u$ on the diagram are recorded according to the data of Dicke and Heath (ref.7). On the basis of a detailed investigation of the first and second positive systems of nitrogen and also on the basis of the rotational analysis of the bands of the Vegard--Kaplan 6--0 and 7 - 0, carried out by Wilkinson (ref.8) these authors again determined the energy of excitation of the indicated states. On the diagram the oscillatory levels of the states $A^3\Sigma_u^+$, $B^3\Pi_g$, $C^3\Pi_u$ are constructed based on data obtained by Dicke and Heath (ref.7) and also by Carroll and Sayers (ref.9) for the succession $\Lambda v = 6$ of the first positive group of nitrogen. The oscillatory levels of states $C^3\Pi_u$ are constructed according to the data of Dicke and Heath (ref.7). The energy of excitation of the state $B^3\Sigma_u^-$ is known from the investigations of the forbidden system of bands $B^3\Sigma_u^- - X^1\Sigma_g^+$ in the ultraviolet region of the spectrum carried out by Wilkinson (ref.10) for the case of absorption and by Ogawa and Tanaka (ref.4) for the case of emission. The oscillatory levels of the state $B^3\Sigma_u^-$ on the diagram is shown according to the data obtained by Wilkinson (ref.10). The energy of excitation of state $^3\Delta_u$ which was not observed experimentally is shown on the diagram on the basis of evaluations carried out by Mulliken (ref.11). The energy of excitation of the quintet state $^5\Sigma_g^+$, which correlates with the basic state $X^1\Sigma_g^+$, is shown on the diagram on the basis of evaluations carried out by Carroll (ref.12) and Mulliken (ref.13). In addition to these states the diagram also shows a large number of electron states with high energies of excitations whose levels were determined as a result

of the investigation of the system of bands by Berge, Hopfield, Gaydon, of the fourth and fifth positive system, the systems of bands of Lofthus, Herman, Kaplan and Goldstein - Kaplan. All of the experimental data pertaining to the indicated states with high energies of excitation are shown in Table 1. In addition to this the diagram shows several states with high energies of excitation, which have not been observed experimentally but which have been predicted theoretically in connection with the work of Mulliken (ref.11). Table 1 shows the values of the oscillatory frequencies and inter-nuclear states for the indicated states obtained on the basis of evaluations carried out by Mulliken (ref.11). In the calculation of thermodynamic functions all the energy levels shown on the diagram (figure 1) may be divided into two groups. The first group contains the states with energies of excitation which are less than $90,000 \text{ cm}^{-1}$. These states, with some difference, were taken into account in the calculation of the thermodynamic functions of molecular nitrogen. The second group contains states with energies of excitation which are greater than $90,000 \text{ cm}^{-1}$. As we can see from the diagram the number of these states is substantial. These states are usually not taken into account in computing the thermodynamic functions. Therefore, as a practical application of this method, it is first of all rational to consider the errors introduced to the calculations of thermodynamic functions of molecular nitrogen when the effect of electron states with energies of excitations greater than $90,000 \text{ cm}^{-1}$ on the values of Q , Q/T , Q''/T^2 are neglected. In solving this problem in addition to

the experimental data shown on Table 1, it is necessary to compute the values of the missing oscillatory states and inter-nuclear distances and also to evaluate the constants of the anharmonic character. We determine the unknown spectroscopic constants using the method proposed by Lippincott, Schroeder, Steele and others (ref.22,23), which have been frequently applied to the N_2 molecule (ref.24-26).

Figure 2 shows the correlation of inter-nuclear distances and oscillatory frequencies for excited electron states of N_2 molecule. The value of the parameter a_i is computed from the experimental values for the oscillatory frequencies and inter-nuclear distances in accordance with equation (ref.25)

$$a_i = 4[1 - \omega_{ei} r_{ei}^2 (1 - 5a/4) / (\omega_e r_e^2)] / 5, \quad a = F / (1 + 5F/4); \quad (1)$$

$$F = a_e \omega_e / 6B_e^2,$$

where ω_{ei} and r_{ei} are oscillatory frequencies and inter-nuclear distances for the i -th excitation and the basic state of the molecule. We can see from figure 2 that the value of the parameter a_i computed from experimental data, for all states investigated spectroscopically, without exception, vary regularly increasing from 0.5 for states with oscillatory frequencies greater than 2000 cm^{-1} , to 0.7 for electron states which are characterized by relatively low stability. We should note that the established correlation is in good agreement with the evaluations of Mulliken (ref.11), which were carried out for states not observed /1738

Table 1

/1737

$$G_x(0) = 1175,7 \text{ cm}^{-1}$$

Nr	Term	ν_e	ω_e	$\omega_e x_e$	B_e	vm	\bar{J}_m	$G_e(0)$	Reference
1	$^2\pi_u$	(94 953)	(450)	(10)	(1,050)	22	85	222,5	[11,14]
2	$E^2\Sigma_q^+$	95 842,8	2218	(16,5)	(1,851)	67	251	1104,9	[11,15]
3	$^1\pi_u$	(98 162)	(2035)	(16,2)	(1,821)	62	240	1013,4	[11]
4	$^1\Sigma_q^+$	(98 372)	(2215)	(17,1)	(1,920)	64	243	1103,2	[11]
5	$C^2\pi_u$	98 508	(500)	(8)	1,0496	31	108	248	[15,16]
6	$i^2\pi_u$	99 319,5	689	(9,4)	(1,220)	36	128	342,2	[17]
7	$r^2\Sigma_u^+$	101 646	(707)	(11)	1,44	32	111	350,8	[17]
8	$b^1\pi_u$	102 274,4	720	(10,8)	1,41	33	116	357,3	[17]
9	$D^2\Sigma_u^+$	103 623,5	(2265)	(17,4)	1,961	65	248	1128,2	[15]
10	$p^1\Sigma_u^+$	104 394,4	2217	19	(1,929)	58	234	1103,8	[18]
11	$b^2\Sigma_u^+$	104 474	751,6	8,26	1,154	45	154	373,7	[19]
12	$d^1\pi_u$	104 790	(2215)	(17,1)	(1,920)	64	243	1103,2	[15]
13	$i^1\pi_u$	104 966,3	(703)	(11,4)	1,494	30	106	348,6	[15]
14	$o^1\pi_u$	105 862	2001	19,275	1,694	51	223	995,7	[20,21]
15	$m^1\pi_u$	106 131,4	785	(10,5)	1,365	37	130	390	[17]
16	$r^1\Sigma_u^+$	106 594,8	(1906)	(15,2)	1,711	62	239	949,2	[11,18]
17	$p^1\pi_u$	108 448,4	770	(10,6)	1,215	36	135	382,4	[17]
18	$d^2\pi_u$	108 875	(2002)	(16)	1,796	62	239	997	[15]
19	$k^1\Sigma_u^+$	109 367,2	(712)	(11)	1,435	32	112	353,2	[11,18]
20	$g^1\Sigma_u^+$	109 778,7	(703)	(10,4)	1,356	33	117	348,9	[15,18]
21	$q^1\Sigma_u^+$	110 653,5	715	9	1,13	39	140	355,2	[17]
22	$s^2\Sigma_u^+$	110 881,3	(1908)	(14,1)	1,595	67	256	950,5	[17]
23	$f^1\pi_u$	110920,1	(913)	(11,5)	(1,493)	39	138	453,6	[17]
24	$r^1\Sigma_u^+$	111 793,7	656	(8,2)	1,07	40	140	326	[17]
25	$h^1\Sigma_u^+$	113029,1	(1849)	(14,7)	1,655	62	240	920,8	[17,18]
26	$x^1\Sigma_q^-$	113 437	1910	20,7	1,750	46	203	949,8	[3-5]
27	$y^1\pi_g$	114 474,9	1740	15,9	1,792	54	203	866	[3-6]
28	$e^1\Sigma_u^+$	115 637	2214	(17,1)	1,92	64	243	1102,7	[15]
29	$x^1\Delta_g$	115 694,4	1700	15,7	1,761	54	205	846,1	[3-6]
30	$^3\Sigma_g^+$	(116 725)	(1910)	(15,6)	(1,759)	61	240	951,1	[11]
31	$^3\Delta_g$	(116 725)	(1910)	(15,6)	(1,759)	61	240	951,1	[11]
32	$^3\pi_g$	(116 730)	(1900)	(15,9)	(1,789)	59	240	946	[11]
33	$^3\Sigma_g^-$	(116 725)	(1910)	(15,6)	(1,759)	61	240	951,1	[11]
34	$s^1\pi_u$	117 591	540	(9,3)	1,11	29	105	267,7	[17]
35	$^1\Sigma_g^+$	(118 725)	(1910)	(15,6)	(1,759)	61	240	951,1	[11]
36	$i^2\pi_u$	119 415	500	(9)	1,16	27	96	247,8	[17]
37	$^1\Sigma_u^+$	119 693	(2450)	(18,7)	(2,103)	65	250	1220,3	[11,15]
38	$^1\Sigma_u^+$	(120 091)	(2179)	(19,1)	(2,142)	57	250	1084,7	[11]

Table 1 (continued)

No.	Term	v_e	ω_e	$\omega_e x_e$	B_e	v_m	\bar{J}_m	$G_i(0)$	Reference
39	$u^1\Sigma_u^+$	121 489	517	7	1,07	39	126	271,8	[17]
40	$1\Sigma_u^+$	121 859	(2177)	(19,1)	(2,141)	56	250	1083,7	[11,15]
41	$v^+?_u$	121 952,4	946	(10,7)	(1,394)	44	155	470,3	[17]

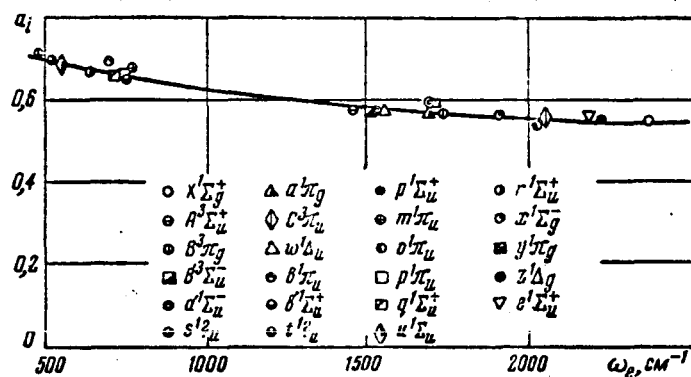


Figure 2. Correlation of inter-nuclear distances and oscillatory frequencies for excited electron states of the N_2 molecule

experimentally. The above regularity in the variation of parameter a_i , together with equation (1), makes it possible to determine immediately the inter-nuclear distances of those states for which the oscillatory frequencies are known, and to evaluate by the method of selection the oscillatory frequencies of states with known inter-nuclear distances. In Table 1 the oscillatory frequencies and rotational constants, taken in brackets, were determined in precisely this manner. In the calculations of ω_{ei} the constant experimental relationship between the parameter a_i and the inter-nuclear distance was also used.

From figure 2 it follows that in view of the stated correla-

tion all of the excited states of the nitrogen molecule may be divided into two groups. It is known from ref.11 that this division of states also has a theoretical basis. There must be a particularly large difference between the states with small oscillatory frequencies and the states with large oscillatory frequencies. Therefore it is natural to expect that by using the same approximate relationship for determining the constant of anharmonic character $\omega_{ei}x_{ei}$ as it applies to all the states will not lead to a good agreement with experimental data. In the present work the constant of anharmonic character for the states with small frequencies was determined by means of Danham's equation (ref.27)

$$\omega_{ei}x_{ei} = B_{ei}(F_i - 1)^2, \quad (2)$$

and for the state with large frequencies was determined by means of the equation proposed by Lippincott and others (ref.24,25)

$$\begin{aligned} \omega_{ei}x_{ei} &= 3B_{ei}[1 + 2F_i^2 / (a_i^2b^2)], \\ F_i &= a_i / (1 - 5a_i/4), \quad b = 1,065. \end{aligned} \quad (3)$$

In the utilization of equation (3) the quantity a_i was assumed to be equal to 0.660 for all states with small ω_{ei} and 0.570 for all states with large ω_{ei} . A comparison of computed and experimentally determined values for the constants of anharmonic character $\omega_{ei}x_{ei}$ is shown in Table 2. /1739

For states $A^3\Sigma_u^+$ and $B^3\Pi_g$, Table 2 shows the constants of anharmonic character computed by us (ref.28) from the

experimental data of Dicke and Heath (ref.7). For the states $a^1\Pi_g, a'^1\Sigma_u^-, w^1\Delta_u, C^3\Pi_u, B'^3\Sigma_u^-$ the values of $\omega_{ci}x_{ei}$ are taken respectively from references (2,5-7,10). The experimental values of the constant of anharmonic character of the states $p^1\Sigma_u^+, o^1\Pi_u, x^1\Sigma_g^-, b'^1\Sigma_u^+, q'^1\Sigma_u^+, u'^1\Sigma_u^+$ are taken from references indicated on Table 1.

Table 2

State	$A^1\Sigma_u^+$	$B^1\Pi_g$	$B'^1\Sigma_u^-$	$a'^1\Sigma_u^-$	$a'^1\Pi_g$	$u'^1\Delta_u$	$C^3\Pi_u$	$p^1\Sigma_u^+$	$o^1\Pi_u$	$x^1\Sigma_g^-$	$b'^1\Sigma_u^+$	$q'^1\Sigma_u^+$	$u'^1\Sigma_u^+$
(experimental)	13,851	14,561	12,22	12,0	13,825	8	26,12	19	19,275	20,7	4,82	9	7
(computed)	13,0	14,6	13,1	13,2	14,4	13,3	16,2	17,2	15,1	15,6	8,3	9,1	8,2
(computed)	13,85	14,94	10,6	9,5	11,6	12,3	20,3	16,6	13,9	12,0			

The last line of Table 2 shows the computed values of $\omega_{ci}x_{ei}$ taking into account various a_1 for each state in accordance with ref.25. As it follows from Table 2, the utilization of various values for a_1 does not lead to a substantial improvement in the agreement between computed and experimentally determined values of $\omega_{ci}x_{ei}$, and in a series of cases this agreement becomes worse, so that it is not rational to apply different values of a_1 . In Table 1 all of the values for the constants of anharmonic character, taken in brackets, were computed using the methodology described above.

The evaluation of the number of oscillatory quanta in each state and also the approximate value of energy of dissociation necessary to determine the limiting values of the rotational quantum numbers J_m was carried out by means of the equations

$$v_{mt} = \omega_{0i} / 2\omega_{0i}x_{0i} \text{ (4)}; \quad D_{ei} = \omega_e^2 / (4\omega_{ei}x_{ei}). \quad (5)$$

The determination of J_m was carried out on the basis of Morse potential function and spectroscopic constants shown in Table 1. It is necessary to point out in view of the adapted methodology that the determination of the limiting number of rotational states is carried out only for the basic oscillatory state corresponding to the given energy of electron excitation. It is known that equation (5) usually leads to higher values both for the energy of dissociation and for the number of oscillatory quanta. The method used in the present work to determine the constants of anharmonic character $\omega_{ei}x_{ei}$ together with equations (5) usually gives a rational number of oscillatory quanta compared with its value for states for which this number is known with a high degree of probability. For this reason in the present work we did not utilize some of the results obtained in ref.25 because the values of the constants of anharmonic character in this work lead to unusually high number of oscillatory quanta for the nitrogen molecule. Also it is necessary to bear in mind that a certain uncertainty introduced into the calculation due to the inaccurate value for the number of oscillatory quanta, computed according to equation (6), is infinitesimally small because the contributions made to Q and especially to Q'/T and Q''/T^2 of the high oscillatory states which have only several rotational levels is insignificant when these are correctly limited. It is necessary to point out that the values of J_m for all oscillatory states determined by means of the

above methodology, except of the principal one, will be somewhat greater than their true values. However, the use of increased values for J_m is expedient, since the situation mentioned partially compensates the error introduced into the calculations because we neglect the correction for the centrifugal extension. Furthermore it is also necessary to bear in mind that the limiting number of rotational states depends on the nature of the forces which bind the molecule, i.e., in the final analysis it depends on the form of the potential function of interaction. An examination of the effect produced by the form of the potential function of interaction on the quantity J_m shows that the values of J_m , computed on the basis of the Morse potential, usually do not vary from the true values by more than 10%. The results of this analysis should be considered in a separate report.

Table 3

$T = 20000 \text{ }^\circ\text{K}, \delta Q = 100 \Delta Q/Q, \%$			
	Q	$-Q'/T$	Q''/T
ΔQ	2745	23540	207300
$X^1\Sigma_g^+, Q_1$	53690	108500	320000
δQ	5,1	21,7	64,8

In the region of energies exceeding $90,000 \text{ cm}^{-1}$, Mulliken (ref.11) theoretically predicted two stable states. Büttner-Bender and Herzberg (ref.14) on the basis of a study of the properties of the dissociation of the upper state $C^3\Pi_u$ of the

second positive nitrogen group determined that the state which produces predissociation must be the ${}^3\Pi_u$ state. Until the present time the bands associated with this state have not been observed in the nitrogen spectrum. According to the evaluation of Herzberg (ref.14), this state must have an energy of excitation, and internuclear distance and an energy of dissociation, respectively, equal to: $\nu_{00} = 94\,000\text{ cm}^{-1}$, $r_e = 1,5\text{ \AA}$, $D_e \cong 5000\text{ cm}^{-1}$. These data were used to evaluate the spectroscopic constants of state ${}^3\Pi_u$. The quantity ω_e computed in accordance with the methodology described above is shown on Table 1. The constant of anharmonic character is determined by means of the equation $\omega_e x_e = \omega_e^2 / 4D_e$. The values ν_m and J_m turned out to be equal to 22 and 85. The indicated state refers to a number of states with low stability. Recently Carroll (ref.16), who analysed the fine structure 0-3, 0-4 and 0-11 of the bands in the system of Goldstein-Kaplan, has shown that the upper state of the system has a term ${}^3\Pi_u$ and not the term ${}^3\Pi_g$ as assumed previously. Carroll also determined the value of the rotational constant which has been used in the present calculations and which is shown on Table 1. Earlier Hamada (ref.29) photographed 13 bands of the Goldstein-Kaplan system and determined the magnitude of the first oscillatory quantum of the upper state equal to $\Delta G = 1395\text{ cm}^{-1}$. However, this value ΔG does not agree with the value of the rotational constant determined by Carroll and contradicts the correlation presented above. In addition to this Gaydon at an earlier date (ref.30) determined the preliminary value of the rotational constant of the upper state for

the system of the Goldstein-Kaplan bands as being equal to 1.1 cm^{-1} which is in good agreement with the value obtained by Carroll (ref.16). On the basis of the analogy CO and N_2 Gaydon expressed the proposition that the oscillatory frequency of state C' must be less than 750 cm^{-1} . In the present work the value of the oscillatory frequency of state C' was evaluated using the method described above in conjunction with the correlation presented on figure 2. The values of v_m and J_m for this state turned out to be equal to 31 and 108, respectively. The state 43 must also be referred to a number of states with low stability. In accordance with the work of Büttenbender and Herzberg (ref.14) it is assumed that state C' does not produce predissociation of the upper state of the second positive group and possibly is itself predissociated under the influence of state 44.

The experimental data of Worly (ref.21) for the state 45 were represented by a two-term equation instead of a $\frac{C'^3\Pi_u}{C'^3\Sigma_u} + \frac{1}{2}$ -term equation as proposed in reference 21.

For a series of states shown on Table 1 the electron terms were not determined. For all the indicated states the statistical weights in calculation were taken equal to 1. /1741

The statistic sums of the excited electron states shown in Table 1 were computed by means of equations which in ref.1 have the following form

$$\begin{aligned}
Q_i &= q_{0i} s_i (1 - r_i \bar{v}_{mi} + u_i x_{0i} \varphi_{2i} + u_i^2 x_{0i}^2 \varphi_{4i} / 2 - I_{0i} / s_i); \\
- Q_i' / T &= q_{0i} s_i \{ 1 - r_i \bar{v}_{mi} + u_i \varphi_{1i} + u_i^2 x_{0i} \varphi_{3i} - u_i^3 x_{0i}^3 \varphi_{5i} / 2 + \\
&\quad + u_i^3 x_{0i}^3 \varphi_{5i} / 2 - u_i^3 x_{0i}^3 \varphi_{6i} / 2 - [I_{0i} (1,5 + \bar{y}_{mi} - a_i^2 / 4b_i) / s_i + \\
&\quad + a_i z_{0i} / (4b_i s_i) - z_{1i} / (2s_i)] \}; \\
Q_i'' / T^2 &= q_{0i} s_i \{ 2 (1 - r_i \bar{v}_{mi} + u_i \varphi_{1i}) + u_i^2 \varphi_{2i} + u_i^3 x_{0i} \varphi_{4i} - \\
&\quad - u_i^3 x_{0i}^3 \varphi_{5i} + u_i^4 x_{0i}^2 \varphi_{6i} / 2 - (I_{0i} / s_i) [1,75 + (1 + \bar{y}_{mi})^2 + \\
&\quad + (1 + \bar{y}_{mi}) (1 - a_i^2 / 2b_i) - a_i^2 (1 - a_i^2 / 4b_i) / 4b_i] - [z_{0i} (1,75 + \\
&\quad + \bar{y}_{mi} - a_i / 8b_i) (a_i / 2b_i) - z_{1i} (1,75 + \bar{y}_{mi} + a_i / 8b_i) + 0,75 a_i z_{2i} - 0,5 b_i z_{3i}] / s_i \}.
\end{aligned}$$

(6)

In spite of the large number of states with high energies (in the calculation 41 states were taken into account), the total volume of calculations in accordance with the proposed method is quite insignificant. The results of calculations are shown on Table 3. For comparison purposes the first line in Table 3 shows the statistical sum of the basic state of the N_2 molecule.

Conclusions

By using the molecular nitrogen, errors are considered which are introduced into calculation of the thermodynamic properties of molecular components when we neglect the contribution to statistical sums of the electron states with high energies of excitation.

On the basis of the calculation of statistic sums in accordance with the proposed method it has been shown that for accurate calculations of thermodynamic properties of molecular components in the region of high temperatures we cannot neglect the contributions indicated above.

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